

Editorial

Catalytic, Photocatalytic, and Electrocatalytic Processes for the Valorization of CO₂

Ilenia Rossetti ^{1,*}  and Gianguido Ramis ² 

¹ Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milan, Italy

² Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, via all'Opera Pia 15A, 16145 Genoa, Italy; gianguidoramis@unige.it

* Correspondence: ilenia.rossetti@unimi.it; Tel.: +39-02-503-14059; Fax: +39-02-503-14300

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Worldwide yearly CO₂ emissions reached 36 Gt in 2014, whereas they amounted to ca. 22 Gt in 1990 [1]. It represents the most abundant greenhouse gas in the atmosphere, 65% of which is derived from direct emissions (combustion and industrial processes), with an additional 11% from the change in land use and forestry [2].

An historic agreement to fight against climate change and move toward a low-carbon, resilient, and sustainable future was agreed by 195 nations in Paris (December 2015). The goal is to keep the temperature rise for the century less than 2 °C and to further limit it to 1.5 °C higher than pre-industrial values. The Intergovernmental Panel on Climate Change [3,4] evidenced an average increase of ca. 0.6 °C on Earth during the 20th century, with an almost exponential rise in the last decade.

Different strategies may be put into place to limit CO₂ output into the atmosphere, e.g., a more efficient use of carbon-based fossil fuels, the use of carbon-less or carbon-free raw materials, and, ultimately, CO₂ capture technologies. However, to be fully effective, carbon dioxide sequestration must be followed by its efficient conversion into useful new materials. This circular approach is virtuous, as it valorizes waste as a new regenerated feedstock, thus limiting the consumption of new sources. In this light, the research has turned from the simpler concept of carbon capture and storage (CCS) to carbon capture and conversion (CCC) or utilization (CCU) [5,6]. This approach moves toward a circular economy approach, perfectly matching the EU and international policies and initiatives.

The first capture step is common: The efficient removal of CO₂ from different point sources, such as the treatment of industrial flue gases, typically in stationary combustion plants, by a separation process, prior to the release of combustion exhausts into the atmosphere. It is much harder to imagine a sequestration method directly by absorption from the atmosphere, as the CO₂ concentration is too low to guarantee a sufficient driving force for its separation.

Several techniques are available for the capture of CO₂ from flue gas [7].

The main approaches are based on:

- i) absorption, either chemical (with ammonia or amines) or physical (Rectisol, Selexol, or Fluor processes), where the selection of the solvent and optimization of the process are key for success [8,9];
- ii) adsorption, usually including the regeneration of the adsorbent through pressure swing or temperature swing adsorption (PSA or TSA) [10];
- iii) cryogenic separation;
- iv) membrane separation (polymeric or ceramic materials);
- v) hybrid technologies.

All of these processes present advantages and disadvantages, which have been very effectively reviewed in a recent paper [11], but the main technology for CO₂ capture is absorption with a liquid solvent (usually alkanolamines [9]) or adsorption in a PSA unit [10].

Once separated, former CCS approaches included planning the confinement of CO₂ into depleted oil and gas wells, deep oceans, and aquifers, or to use it as a fluid for fuel extraction (e.g., its injection in geological formations and the subsequent recovery of fuel products with several techniques, such as enhanced oil recovery, enhanced coal bed methane recovery, enhanced gas recovery). However, as said, much more effective approaches are needed to try to recover valuable products from its conversion through a circular economy vision [12].

In addition, in this case, different strategies are under development, leading to various upgraded products. Some conversion routes are oriented toward the regeneration of fuels, which can, in general, be defined as C_xH_yO_z. The energy required for CO₂ reduction increases more and more while decreasing *z* and increasing *x*, while the stored energy in the regenerated fuel increases accordingly. This approach is usually convenient when inexpensive renewable energy is available. In addition, it is a circular path, as the main CO₂ emissions come from combustion, and fuels are regenerated to be used in the same market. Provided a sufficiently efficient and cost-effective technology for fuel regeneration from CO₂ can be developed, the potential market for regenerated fuels matches the huge CO₂ emission volume. The opposite holds for rival pathways that tend to valorize CO₂ in fine chemicals or value-added products. If, on the one hand, the remunerability of the product is much higher, and can economically support the development of the technology, the size of the potential market of these fine chemicals can hardly match the volume of CO₂ emissions, needing the development of a network of parallel CCU technologies.

Among the different pathways, biological methods have been developed, either directly producing reduced products [13] (i.e., carbonic anhydrase, hydrogenation of CO₂ to formate, reduction of CO₂ to methane, CO₂ conversion into methanol by enzyme cascade) or storing CO₂ in biomass (e.g., algae) [14], to be subsequently upgraded.

The electrochemical reduction of CO₂ can be effectively exploited through available renewable electricity. For instance, CO₂ can be electrochemically reduced to formic acid derivatives that can subsequently be converted into useful monomers, such as glycolic acid and oxalic acid, to be employed as building blocks for polyesters [15]. The potential of CO₂ electroreduction to methane has been recently reviewed by Zhang et al. [16].

Photocatalytic reduction allows the production of a wide spectrum of products, such as HCOOH, HCHO, CH₃OH, or CH₄ [17–23], and can be effectively used for the exploitation of solar energy, provided visible responsive materials can be developed for this application [24].

Furthermore, the catalytic reduction of CO₂ has been proposed through the Sabatier reaction [25]. The methane produced in this reaction has great potential for application, but the application of this technology relies on the availability of renewable and inexpensive H₂. A different approach is the methanation of CO₂ through biochemical approaches.

This Special Issue

Different options of CO₂ valorization have been discussed in this special issue, showing interesting examples of the catalytic science impact in this important field. At first, the potential for the catalytic methanation of CO₂ was reviewed by Manzoli and Bonelli [26], who discussed the importance of catalyst design to ensure efficient performance in the (photo)catalytic hydrogenation of CO₂. Different enabling technologies assisting catalyst synthesis (microwaves, ultrasound, mechanochemical synthesis) allow tailored properties for the selected materials to be obtained, which, in turn, ensures suitable catalyst performance.

The methanation of CO₂ was studied under unsteady conditions to evidence the structural dynamics of the Ni/Al₂O₃ catalyst [27]. Different operando characterization techniques were used, such as Quick-scanning X-ray Absorption Spectroscopy/Extended X-ray Absorption Fine Structure

(XAS/QEXAFS) considering stops in the H₂ supply during the reaction while feeding oxidizing impurities to simulate the technical purity of CO₂.

Methanation has also been investigated through sorption-enhancement [28], which allows faster production of pure methane thanks to the application of Le Châtelier's principle. The long-term stability of a catalyst, constituted by Ni nanoparticles supported on zeolite 5A, has been examined and showed to be satisfactory thanks to milder operating conditions of the sorption-enhanced process with respect to the conventional one. A degradation mechanism specific to the sorption catalysis was derived on the basis of cyclic methanation/drying periods and was related to the water diffusion kinetics in the zeolite. The latter step is rate controlling during both methanation and drying, so this point is kinetically critical.

An example of the electro-reduction of CO₂ was proposed by Castelo-Quibén et al. [29], obtaining C1 to C4 hydrocarbons, as an efficient strategy for C–C coupling. The electroactive materials were composite metal–carbon–carbon nanofibers synthesized using urban plastic residues through catalytic pyrolysis. Selectivity was tunable by changing the metal.

The photoreduction of CO₂ was investigated under unconventional operating conditions, i.e., at high pressure and high temperature [21], using different TiO₂-based catalysts and investigating the effect of different reaction parameters. A significant productivity of liquid-phase products (HCOOH and HCHO) was achieved. The selectivity to different products was tuned based on pH, reaction time, and through the addition of Au nanoparticles as a co-catalyst.

Finally, the synthesis of dimethylcarbonate (DMC) was investigated by Han et al. [30,31]. Different alkali metals were added to Cu–Ni/diatomite catalysts to synthesize DMC from CO₂ and methanol, thanks to their strong electron-donating ability. Cs₂O was effective, leading to a ca. 10% methanol conversion with a ca. 86% selectivity to DMC [31]. Furthermore, the same authors investigated the effect of dehydration using 3A molecular sieves to shift the equilibrium and to improve the stability of a K₂O-promoted Cu–Ni catalyst [30]. An improved yield of DMC by 13% was obtained with respect to the undehydrated base case and stable performance for 22 h.

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